

The University of Chicago

EFFECT OF SUBSTITUENTS ON THE
ELECTRONEGATIVITY OF THE
NAPHTHYL RADICALS

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1937

By

SYLVIA KRAMER

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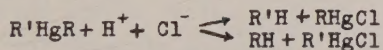


OBJECT OF THE WORK

The object of this investigation is to extend the present table of "Relative Order of Electronegativities of Organic Radicals" to the naphthalene series and to determine whether substituents affect the electronegativity of the naphthyl radical in the same manner as they do the phenyl radical.

STATEMENT OF THEORY AND METHOD OF ESTABLISHING RELATIVE ELECTRONEGATIVITY

"Electronegativity" is a term proposed by Kharasch and his co-workers to denote the relative affinity of a radical for a pair of valence electrons. The more negative this affinity the more electronegative the radical. This attraction is, of course, determined by the nature of the molecule; hence radicals differ in electronegativity. The relative electronegativity of radicals is determined by Kharasch and Marker.² The unsymmetrical organic mercury compound with hydrogen chloride. One or both of the reactions indicated below may take place:



The more electronegative radical is defined as that one which combines with the hydrogen ion to form the hydrocarbon.

When the two radicals comprising the unsymmetrical compound differ greatly in relative electronegativity, the decomposition proceeds quantitatively to give only one organomercuric halide. However, if the two radicals R and R' differ but slightly in relative electronegativity, both organomercuric halides are formed, but the reaction product contains a larger proportion of

¹For a full discussion of this concept see; M. S. Kharasch and R. Marker, J. Am. Chem. Soc., **48**, 3130 (1926); M. S. Kharasch and O. Reinmuth, J. Chem. Ed., **5**, 404 (1928); M. S. Kharasch and A. L. Flenner, J. Am. Chem. Soc., **54**, 674 (1932).

²M. S. Kharasch and R. Marker, op. cit.

the organomercuric halide of the less electronegative radical.

By suitably varying the radicals R and R' the electronegativities of a great variety of organic radicals have been compared by Kharasch and his co-workers. These radicals have been arranged according to their electronegativities for the purpose of correlating the reactivities of organic compounds.

HISTORICAL PART

The first authentic report on the preparation of unsymmetrical organic mercury compounds was made by Hilpert and Grüttner.¹ They prepared these compounds by treating an alkyl- or arylmagnesium halide with the corresponding organomercuric chloride. Thus, they prepared phenyl mercury benzyl by treating phenylmagnesium bromide with benzylmercuric chloride. They state that by the use of this method such unsymmetrical compounds can be prepared only from appropriate Grignard reagents. Thus in the preparation of phenyl mercury ethyl they used the Grignard reagent of phenyl bromide and in the preparation of benzyl mercury ethyl they used the Grignard reagent of ethyl bromide. When the Grignard reagents of ethyl bromide and benzyl bromide were used in the preparation of these two compounds, only symmetrical compounds were obtained. They decided that to obtain the unsymmetrical compounds the Grignard reagent of the radical having the smaller affinity for mercury must be used. They therefore listed phenyl, ethyl, benzyl in the order of their increasing affinity for mercury. This is exactly the order of the decreasing electronegativity of the radicals as determined by Kharasch and his co-workers.

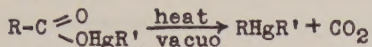
These latter workers, however, found that the Grignard reagent of either radical could be used when other factors are controlled. If the temperature is kept low and not too great an excess of Grignard reagent is used, all types of unsymmetrical organic mercury compounds may be prepared.

Another method of preparing unsymmetrical organic mercury compounds is described by Kharasch and his co-workers.² This method consists in the elimination of carbon dioxide from molecules of the type $\text{R}-\text{C} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{OHgR}' \end{smallmatrix}$ in which $\text{R}-\text{C} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{OH} \end{smallmatrix}$ represents an acid

¹S. Hilpert and G. Grüttner, Ber., **48**, 906 (1915).

²M. S. Kharasch, J. Am. Chem. Soc., **43**, 2238 (1921); M. S. Kharasch and F. W. Stavely, J. Am. Chem. Soc., **45**, 2961 (1923); M. S. Kharasch and M. W. Grafflin, J. Am. Chem. Soc., **47**, 1948 (1925).

which loses carbon dioxide readily. The reaction takes place in the following manner:



PROOF OF STRUCTURE OF R-Hg-R'

Since unsymmetrical and mixtures of symmetrical organomercury compounds may possibly yield the same products on treatment with hydrogen chloride it is necessary to prove that a compound has the unsymmetrical structure. The following criteria were used by Kharasch and Flenner¹ to prove the structure of the unsymmetrical molecule:

1. Determination of the per cent of mercury.

2. Treatment with an equivalent amount of mercuric chloride. This reaction yields two organomercuric chlorides according to the following equation:



These organomercuric chlorides are isolated wherever possible and identified.

3. Treatment with alcoholic hydrogen chloride.

The mercury analysis establishes the purity of the compound. It does not however, indicate whether the material is an unsymmetrical compound or an equimolecular mixture of two symmetrical compounds. The burden of proof of the unsymmetrical structure rests upon the products obtained in the decomposition with mercuric chloride and with hydrogen chloride. If the material yields two organomercuric chlorides on treatment with mercuric chloride and only one on treatment with hydrogen chloride the presence of the unsymmetrical molecule is indicated. However, if the compound yields two organomercuric halides, both on treatment with mercuric chloride and with hydrogen chloride, the presence of the unsymmetrical structure is not demonstrated. In this case the same products would be obtained if the material is an unsymmetrical molecule or if it is a mixture of two symmetrical ones. Criteria such as melting point, solubility, etc., may help distinguish an unsymmetrical compound from a mixture. However, even these criteria fail in certain cases because some unsymmetrical compounds are

¹M. S. Kharasch and A. L. Flenner, J. Am. Chem. Soc., **54**, 674 (1932).

difficult to purify and rearrange in solution to give two symmetrical molecules.

Another avenue of approach presents itself from a consideration of the amounts of materials obtained by the hydrogen chloride decomposition. If the compound is unsymmetrical, treatment with hydrogen chloride can yield a maximum of one equivalent of organomercuric chloride, but if the material is an equimolecular mixture only one half an equivalent can be obtained since the other half forms the hydrocarbon. If the radicals differ greatly in weight, these differences could be detected in the weights of the mercuric chlorides obtained in the hydrogen chloride decomposition. But in most cases these differences are too small for detection by other than quantitative methods which have not been worked out thus far.

On the whole the proof of structure of those unsymmetrical compounds which yield two organomercuric chlorides on treatment with hydrogen chloride is based on analogy with the class of unsymmetrical compounds which yield only one organomercuric chloride on such treatment.

RESULTS AND CONCLUSIONS

Although much work has been done by Kharasch and his co-workers on the electronegativities of the substituted benzenes, only one unsymmetrical compound involving naphthalene has been prepared, α -naphthyl mercury phenyl.

The choice of radicals to be used for comparison in this work was limited by the difficulty of preparation and by the necessity of proving the structure of the compounds obtained. Such proof is impeded by the relatively few substituted naphthalenes known.

In this investigation the following compounds were prepared:

1. α -Naphthyl mercury β -naphthyl
2. 4-Chloro-1-naphthyl mercury α -naphthyl
3. 5-Bromo-1-naphthyl mercury α -naphthyl
4. 2-Methoxy-1-naphthyl mercury α -naphthyl
5. 4-Chloro-1-naphthyl mercury phenyl.

The electronegativity of these substituted naphthyl radicals in general follows the order that would be predicted on the

basis of the information available from the benzene series.

The work of Kharasch and Marker¹ has already established the position of the α -naphthyl radical in the phenyl series. These workers have shown that the naphthyl radical is more electronegative than the phenyl radical.

Within the naphthalene series itself, the relation between the α - and β -naphthyl radicals was first determined. From the greater reactivity of the alpha position in substitution and other reactions, one would predict that the α -naphthyl radical would be the more electronegative. Results have shown this assumption to be correct. α -Naphthyl mercury β -naphthyl on treatment with hydrogen chloride yields a mixture of arylmercuric chlorides which analyzes 80% β -naphthylmercuric chloride and 20% α -naphthylmercuric chloride.

Substituents introduced into the naphthalene ring affect the electronegativity of the radical in the same manner as do substituents in the benzene ring. A chlorine atom introduced in the naphthalene ring lowers the electronegativity of the radical. Thus the action of hydrogen chloride on 4-chloro-1-naphthyl mercury α -naphthyl yields a mixture composed of 75% 4-chloro-1-naphthylmercuric chloride and 25% α -naphthylmercuric chloride. This experiment shows the naphthyl radical to be more electronegative than the 4-chloro-1-naphthyl radical.

Since α -naphthyl mercury phenyl, on treatment with hydrogen chloride yields 100% phenylmercuric chloride, and 4-chloro-1-naphthyl mercury α -naphthyl yields 75% 4-chloro-1-naphthylmercuric chloride, it can be predicted that the 4-chloro-1-naphthyl radical is more electronegative than the phenyl radical. This is shown to be the case when 4-chloro-1-naphthyl mercury phenyl is treated with hydrogen chloride. A mixture composed of 65% phenylmercuric chloride and 35% α -naphthylmercuric chloride is obtained.

The effect of an halogen on the electronegativity of the naphthyl radical when the halogen and the mercury are situated in two different rings was then determined. The 5-bromo-1-naphthyl mercury α -naphthyl was prepared. On treatment with hydrogen chloride it yields a mixture of arylmercuric chlorides which analyzes 25% α -naphthylmercuric chloride and 75% 5-bromo-1-naphthyl-

¹M. S. Kharasch and R. Marker, op. cit.

mercuric chloride. The α -naphthyl radical is thus shown to be more electronegative than the 5-bromo-1-naphthyl radical. Although the halogen is introduced into the second ring it still lowers the electronegativity of the radical.

The effect of a methoxy group on the electronegativity of the naphthyl radical was then determined. In the benzene ring the effect of a methoxy group is opposite to that of an halogen, since the methoxy group increases the electronegativity of the radical. 2-Methoxy-1-naphthyl mercury α -naphthyl was prepared. On treatment with hydrogen chloride it yields a mixture composed of 27% 2-methoxy-1-naphthylmercuric chloride and 73% α -naphthylmercuric chloride. The conclusion drawn from this experiment is that the 2-methoxy-1-naphthyl radical is more electronegative than the α -naphthyl radical. These results indicate that the two types of substituents, exemplified by the halogens and the methoxy group, have the same effect on the naphthyl radical as they do on the phenyl radical.

The fact that the 4-chloro-1-naphthyl radical is more electronegative than the phenyl radical indicates that the chlorine atom does not depress the electronegativity of the naphthyl radical as much as it does the phenyl radical. An alternative explanation is that the electronegativity of the naphthyl radical is so very much greater than that of the phenyl radical that even a large depression by a halogen would not lower its electronegativity below that of the phenyl radical.

It is interesting to note that the substituents in the second ring still extend an influence in the same direction and of similar magnitude as substituents in the first ring. Perhaps an explanation of this fact may be that the substituents in both rings are in the alpha positions. There also does not seem to be an appreciable difference between the effect of the chlorine and the bromine atom. This is in agreement with the results obtained by Pines¹ on the corresponding benzene derivatives.

¹H. Pines, Doctor's Dissertation, University of Chicago, 1936.

EXPERIMENTAL PART

METHOD OF ANALYSIS FOR MERCURY

The analysis for mercury in this study is important not only in determining the purity of both the arylmercuric chlorides and unsymmetrical mercury compounds prepared, but also in the determination of relative electronegativities. These, in most cases, are determined by analysis of a mixture of the arylmercuric chlorides resulting from the hydrogen chloride cleavage of the unsymmetrical compound. The method of Whitmore and Sobatzki,¹ given below, is both simple and accurate.

About 0.1 g. of mercuri bis compound or 0.2 g. of organo mercuric halide, weighed accurately, is mixed with 1 g. of potassium iodide, 2 cc. of chloroform, 25 cc. of water and 25 cc. of approximately 0.1 N. iodine solution in a 100 cc. Erlenmeyer flask attached to a reflux condenser by a ground joint. The flask is heated sufficiently to cause the chloroform to reflux gently for 15-30 minutes. During the refluxing 25 cc. of the iodine solution used is titrated with accurately standardized sodium thiosulfate solution (approximately 0.05 N). The flask containing the reaction mixture is cooled, acidified with two drops of concentrated hydrochloric acid and titrated with the standard thiosulfate. The difference in the thiosulfate used here and with the blank iodine titration gives a measure of the C-Hg linkage present, each such linkage corresponding to two equivalents of iodine or thiosulfate.

PREPARATION OF ARYLMERCURIC CHLORIDES

Since a variety of methods was used in preparing the six arylmercuric chlorides for this work, each will be described in detail.

I. α -Naphthylmercuric Chloride

This compound was prepared in three different ways.

By direct mercuration of naphthalene with mercuric acetate and subsequent treatment with sodium chloride.²--The compound obtained by the long series of extractions of this method could

¹F. C. Whitmore and R. J. Sobatzki, J. Am. Chem. Soc., **55**, 1131 (1933).

²O. Dimroth, Ber., **35**, 2036 (1902).

not be sufficiently purified.

By means of the reaction of the sulfinic acid with mercuric chloride.--This reaction is described in greater detail. α -Naphthalenesulfinic acid was prepared by a modification of the method of Otto.¹ Enough alcohol was added to 30 g. of zinc dust to make it into a paste. The mixture was gently heated on the water bath and continually stirred as 36 g. of α -naphthalenesulfonyl chloride was slowly added. The mixture was kept in the condition of a thin paste by the frequent addition of alcohol. After all of the α -naphthalenesulfonyl chloride was used up, 300 cc. of 1 M sodium carbonate was added and the alcoholic solution separated from the solids by filtration. The filtrate was evaporated to about one-third its volume and cooled. The free sulfinic acid was precipitated by the addition of an excess of dilute hydrochloric acid. Yield, 21 g.; calculated, 31 g. The compound, crystallized from alcohol, melted at 104-6°. It is important to avoid overheating the reaction mixture, and to add the α -naphthalenesulfonyl chloride slowly.

In another preparation of this compound, 82 g. of α -naphthalenesulfonyl chloride yielded 66 g. of acid melting at 101-3°. Many different melting points are recorded for this compound. Concentrated sulfuric acid is a reliable reagent which differentiates the naphthalenesulfinic from the sulfonic acids. α -Naphthalenesulfinic acid gives first a blue and then a green color. The β -naphthalenesulfinic acid gives a green color directly.

The sulfonyl chloride was prepared by the standard method. Ten parts of sodium naphthalenesulfonate, thoroughly dried at 180°, was mixed with six parts of phosphorus pentachloride. The mixture was heated for four hours at 125°, cooled and treated with ice and water. The solid was collected on a filter and crystallized from alcohol. From 125 g. of sodium α -naphthalenesulfonate, 134 g. of the crude sulfonyl chloride was obtained. On crystallization from alcohol, 82 g. of material melting at 65-66° was obtained.

Reaction of α -Naphthalenesulfinic acid with mercuric chloride was accomplished in the following manner. The α -naphthalenesulfinic acid was dissolved in alcohol. The equivalent

¹R. Otto, A. Rossing and J. Troger, J. pr. Chem. (2) 47, 95 (1893).

amount of mercuric chloride was dissolved in hot water. The solutions were mixed and the mixture warmed for half an hour on the water bath. The white precipitate which separated was collected on a filter and crystallized from hot benzene. From 33 g. of the sulfinic acid 32 g. of α -naphthylmercuric chloride was obtained. The melting point of the material was 188-90°.

The Grignard reaction.--The Grignard reaction affords an excellent method of preparing α -naphthylmercuric chloride. The yield of the organomercury halide is high and the product is pure. In the preparation of the Grignard reagent, 4.8 g. of magnesium was covered with about 75 cc. of ether. To this mixture 41 g. of α -naphthyl bromide dissolved in 150 cc. of ether was slowly added. The reaction is easily initiated by the addition of a drop of methyl iodide. When the reaction was complete 54 g. of dry mercuric chloride was added in small portions while the reaction mixture was vigorously stirred. When all of the reagent had been added, the mixture was stirred and refluxed for two hours longer. The solid formed was collected on a filter and washed with hot water and a little dilute acid until the filtrate gave no test for mercuric ion when treated with sodium hydroxide. The reaction yielded 80 g. of crude material which diminished to 55 g. on crystallization from hot refined fusel oil (mixture of amyl alcohols). The melting point of the material was 188-90°.

II. β -Naphthylmercuric Chloride

This material was prepared from the corresponding sulfinic acid in exactly the same manner as described for the alpha isomer, but the β -naphthylmercuric chloride obtained by this method could not be completely purified. Evidently the starting material, β -naphthalenesulfonic acid, contained some of the alpha isomer.

β -Naphthylmercuric chloride was obtained pure by means of the Grignard reaction. The procedure employed was the one described for the preparation of α -naphthylmercuric chloride. The β -bromonaphthalene used in preparing the Grignard reagent was obtained by heating an equimolecular mixture of β -naphthol and phosphorus pentabromide in a bomb tube for 10-12 hours at 150°. The contents of the bomb were poured into water, washed with a solution of sodium hydroxide and purified by steam distillation.

The Grignard reagent of β -bromonaphthalene is more difficult to prepare than that of the alpha compound. If, however,

the β -bromonaphthalene is freshly crystallized and dry, it will react easily with the magnesium, particularly on the addition of a drop of methyl iodide.

It is more difficult to initiate the reaction of magnesium with the naphthyl halides than with the corresponding phenyl derivatives. The reaction is more sluggish and often the reaction mixture requires heating. The naphthylmagnesium halides are also more insoluble in ether. To keep them in solution a larger volume of ether must be used, even though such dilution diminishes the speed of the reaction. More concentrated ether solutions of the naphthylmagnesium halides may be obtained if stirring is not used in their preparation.

From 10 g. of β -bromonaphthalene, 10 g. of β -naphthylmercuric chloride was obtained which melted at 263° . Upon crystallization, first from amyl alcohol and then from hot benzene, the compound was obtained in glistening flakes which melted at $269-70^{\circ}$.

In another experiment, 20 g. of β -bromonaphthalene yielded 30 g. of β -naphthylmercuric chloride whose melting point was $250-55^{\circ}$. After crystallization from refined fusel oil, the melting point of the material was raised to 271° .

III. Phenylmercuric Chloride

This compound was prepared from phenylmagnesium bromide and mercuric chloride. The method yielded a mixture of phenylmercuric chloride and phenylmercuric bromide but since this does not affect the subsequent reaction, the material was used as such.

IV. 4-Chloro-1-naphthylmercuric Chloride

Direct mercuration.--The preparation of a chloronaphthylmercuric chloride was first attempted by direct mercuration of α -chloronaphthalene. A ratio of five moles of α -chloronaphthalene to one of mercuric acetate was used. No reaction takes place when a solvent (alcohol) is used no matter how long and how vigorously the mixture is boiled.

To 8 g. of α -chloronaphthalene 3.5 g. of dry mercuric acetate was added and the mixture heated until a clear solution resulted. An excess of a water solution of sodium chloride was then added and the mixture again warmed for 10 minutes. The precipitate which formed was collected on a filter and washed with

water until the washings showed no test for chloride ion. The white powdery material was then boiled with alcohol to remove the excess α -chloronaphthalene. The melting point of the compound so obtained, $137-60^{\circ}$, indicated that it was not pure. It was not soluble to any extent in the ordinary solvents except pyridine. However, it was too soluble in this solvent for crystallization purposes. Neither could pyridine be used as a solvent from which the compound could be precipitated, for the precipitate was too fine to be held by even a sintered glass filter. Furthermore, as will be shown later, pyridine reacts with organomercury compounds. In spite of the lack of purification the analysis of this compound showed it to be that of a chloronaphthylmercuric chloride. The impurities present were probably isomers.

Analysis: Calc. for $C_{10}H_6HgCl_2$; Hg, 50.47%. Found; Hg, 50.12%, 51.04%.

Grignard reaction.--The Grignard reaction was used in the preparation of 1:4 chloronaphthylmercuric chloride.

1-Bromo-4-chloronaphthalene was first prepared by a modification of the procedure of Guareschi and Biginelli.¹ α -Chloronaphthalene is treated directly with one mole of bromine. The reaction is strongly exothermic. The product yields a yellowish solid when poured on ice. A single crystallization from alcohol yields pure material. From 26 g. of α -chloronaphthalene and 26 g. of bromine, 15 g. of pure 4-chloro-1-bromonaphthalene was obtained. The melting point of the compound is $65-66^{\circ}$.

Although 4-chloro-1-naphthylmagnesium bromide is not reported in the literature, it is quite easy to prepare. 4-Chloro-1-bromonaphthalene (12 g.) dissolved in 10 cc. of ether was added to 12 g. of magnesium covered with about 25 cc. of ether. A vigorous reaction ensued upon the addition of a few drops of methyl iodide. The reaction was continued with slight heating for four hours. The amount of Grignard reagent was determined by treating an aliquot portion with a known quantity of sulfuric acid and titrating back the excess with sodium hydroxide. Upon this basis the yield of the organomagnesium compound was 95% of the calculated. This Grignard reagent was added slowly to 13.5 g. of mercuric chloride dissolved in about 300 cc. of dry ether. This procedure was used in order to prevent the formation of chloronaph-

¹J. Guareschi and P. Biginelli, Bull. (2) 49, 556 (1888).

thylmercuric bromide which is sometimes formed when the solid mercuric chloride is added to the Grignard reagent. After allowing the reaction flask to stand over night (two hours refluxing was later employed) it was treated with ice and 1% sulfuric acid. The solid was collected and washed with water until the washings gave no test for mercuric ion. Weight 9 g. (50% yield). Crystallization from hot benzene yielded 6 g. of a white material which melted at 230-1°. The analysis for mercury, however, was 5% too low. On recrystallizing the material from benzene its melting point was raised to 239-40° and an analysis for mercury showed the compound to be pure chloronaphthylmercuric chloride.

Analysis: Calc. for $C_{10}H_6HgCl_2$; Hg, 50.47%. Found; Hg, 50.79%, 50.20%.

In another experiment the Grignard reagent was prepared in the following manner. To 7.2 g. of magnesium, suspended in 60 cc. of ether, 72 g. of 1-bromo-4-chloronaphthalene dissolved in 150 cc. of ether was added. The Grignard reagent formed was added to an ether solution of 80 g. of mercuric chloride. The mixture was then refluxed for an hour. Further treatment was as described above. Yield 87 g. M.P. 230-4°. Crystallization from amyl alcohol yielded 40 g. of a product melting at 239-40°.

When the compound was prepared by adding solid mercuric chloride to the Grignard reagent of 4-chloro-1-bromonaphthalene, a material was obtained which was a mixture of 4-chloro-1-naphthylmercuric chloride and 4-chloro-1-naphthylmercuric bromide.

V. 5-Bromo-1-naphthylmercuric Chloride

This compound could not be prepared by means of the Grignard reagent because the starting material, 5-bromo-1-chloronaphthalene, was difficult to obtain. Although Guareschi and Biginelli¹ claim to have obtained it by direct chlorination of α -bromonaphthalene, the 5-bromo-1-chloronaphthalene could not be isolated from the other isomers formed in the reaction mixture.

The 5-bromo-1-naphthylmercuric chloride was prepared by the following series of reactions.

α -Nitronaphthalene was prepared according to directions of Aquir.² It is essential, because of its subsequent use, to prepare this substance quite pure. The following procedure was

¹ Ibid.

² A. A. de Aquir, Ber., 5, 370 (1872).

found quite adequate. The naphthalene is dissolved in glacial acetic acid. An equivalent amount of ordinary nitric acid is added and the mixture boiled for one-half hour. On cooling α -nitronaphthalene separates and is crystallized from alcohol. It is necessary to repeat this crystallization several times to insure a pure product. From 128 g. of naphthalene, 100 g. of pure α -nitronaphthalene was obtained.

5-Bromo-1-nitronaphthalene was prepared by a slight modification of the directions given by Guareschi.¹ The method consists in adding dropwise the molecular equivalent of bromine to solid α -nitronaphthalene. Addition of an excess of bromine produces dibromo derivatives. At first there is no apparent reaction. However, as more bromine is added a vigorous reaction ensues. Large quantities of hydrogen bromide are evolved, heat is liberated and the mass within the flask becomes fluid. To facilitate the removal of hydrogen bromide, air is passed through the mixture. The same result may be achieved by warming the reaction mixture on a steam bath. If pure α -nitronaphthalene is used the molten mass solidifies easily and the yield of 5-bromo-1-nitronaphthalene is high. The melting point of the crude material is 115° . The melting point of the pure product as reported by Guareschi is 122.5° . From 100 g. of slightly impure α -nitronaphthalene only 25 g. of pure 5-bromo-1-nitronaphthalene was obtained. In another experiment 50 g. of pure α -nitronaphthalene yielded 50 g. of 5-bromo-1-nitronaphthalene.

5-Bromo-1-naphthylamine was prepared by the reduction of 5-bromo-1-nitronaphthalene with stannous chloride according to the directions of Ullmann and Consonno.²

To a hot solution of 14 g. of stannous chloride in a mixture of 20 cc. of concentrated hydrochloric acid and 25 cc. of alcohol, 5 g. of nitrobromonaphthalene are added a little at a time. From the clear liquid the alcohol is removed by distillation. Upon cooling, especially on addition of fuming hydrochloric acid, the double tin salt crystallizes in small slightly yellow needles.

This product is pressed on a filter and without drying suspended in water. Sodium hydroxide is then added until the solution is distinctly alkaline and the bromonaphthylamine is extracted with ether. The amine is readily oxidized by air and turns dark. It

¹J. Guareschi, Ann., 222, 294 (1883).

²F. Ullmann and F. Consonno, Ber., 35, 2804 (1902).

keeps quite well, however, in the form of its salts. The hydrochloride was obtained by adding a small quantity of hydrochloric acid in alcohol solution to the ether extract. The color of the freshly precipitated amine hydrochloride is white.

From 30 g. of 5-bromo-1-nitronaphthalene, 18 g. of 5-bromo-1-naphthylamine hydrochloride was obtained. In another experiment, 40 g. of the nitrobromo compound yielded 21 g. of the amine hydrochloride. When heated the material darkens at 224° and melts with decomposition at 262° .

The hydrochloride may be purified by dissolving in slightly acidulated water and precipitating by the addition of concentrated hydrochloric acid.

5-Bromo-1-naphthylidiazonium chloride -- mercuric chloride double salt was obtained through diazotization of the amine hydrochloride prepared above. To 19 g. of the amine hydrochloride suspended in a mixture of 30 cc. of concentrated hydrochloric acid and 45 cc. of water, 90 g. of ice is added and then 4.8 g. of sodium nitrite dissolved in 5 cc. of water. The nitrite is added to the mixture dropwise and with stirring. The resulting solution of the diazonium salt is filtered directly into a solution of 26 g. of mercuric chloride in 100 cc. of alcohol. A chartreuse colored material precipitated. It was collected on a filter and washed with alcohol. It melts at 121° with decomposition. Yield 11.5 g. In another experiment 45 g. of 5-bromo-1-naphthylamine hydrochloride yielded 30 g. of the double salt. The salt contains a great deal of adsorbed water which is difficult to remove by suction. It must be dried below 50° to avoid explosion.

Nesmejanow reaction.¹ This reaction involves the decomposition of the diazonium mercuric chloride double salt in the presence of metals like copper or mercury. In the reaction the -HgCl radical takes the place originally occupied by the nitrogen atom. Thus the position of the mercury in the ring is known. Nesmejanow used catalytic copper to affect this reaction but Kharasch and Pines² have found that a smoother reaction, better yields and products freer from side reactions are obtained when mercury is used instead of copper. The reaction takes place in the following manner:

¹A. N. Nesmejanow, Ber., 62, 1010 (1929).

²H. Pines, op. cit.



In one experiment 4.5 g. of the diazonium mercuric chloride double salt was suspended in 200 cc. of acetone and 40 g. of mercury added. After half an hour bubbles of nitrogen began to evolve and the solution was colored red. After standing at room temperature for 20 hours, evolution of nitrogen ceased and the solid at the bottom of the flask had completely changed in appearance. The chartreuse color of the diazonium mercuric chloride double salt was replaced by the grayish-white color of mercurous chloride. The supernatant liquid was dark red. It was decanted. The solid was extracted with more acetone and the acetone extracts combined. The 5-bromo-1-naphthylmercuric chloride was precipitated from the acetone solution by addition of water and purified by two crystallizations from hot benzene.

The reaction could be brought to completion much more quickly and with less decomposition by stirring the reaction mixture. On such treatment evolution of nitrogen ceased after 5-6 hours. The supernatant liquid was light yellow in color and the material obtained from it could be more easily purified. From 30 g. of the diazonium mercuric chloride double salt, 15 g. of the crude bromonaphthylmercuric chloride was obtained which yielded 4 g. of pure material. The substance melts with decomposition at 228° .

Analysis: Calc. for $\text{C}_{10}\text{H}_6\text{HgClBr}$; Hg, 45.39%. Found; Hg, 44.95%, 45.05%, 44.76%.

It will be noticed that this melting point is about the same as that of 4-chloro-1-naphthylmercuric chloride, although one might expect the melting point to be quite different since the halogen and the $-\text{HgCl}$ radical are in two different rings. 5-Bromo-1-naphthylmercuric chloride is somewhat more soluble than 4-chloro-1-naphthylmercuric chloride in benzene, acetone and alcohol.

VI. 2-Methoxy-1-naphthylmercuric Chloride

Methylation.--The first attempt to prepare this compound was made through the methylation of 2-hydroxy-1-naphthylmercuric chloride. The latter compound is easily prepared by treating the sodium salt of β -naphthol with mercuric chloride.

The sodium salt of β -naphthol was prepared by dissolving 58 g. of β -naphthol in 100 cc. of water containing an equivalent

amount of sodium hydroxide (16 g.). The sodium salt solution was filtered and slowly added to a hot aqueous solution of 109 g. of mercuric chloride. The yellow material first formed on contact of the two liquids disappears and a white solid separates. The material is collected on a filter and washed several times with water. Yield 140 g. Calc. 153 g.

Purification was effected by dissolving the compound in very dilute sodium hydroxide and precipitating with acetic acid. The melting point of the material so obtained was $174-5^{\circ}$ with decomposition. The melting point of this compound is not recorded in the literature.

2-Hydroxy-1-naphthylmercuric chloride could not, however, be methylated by the following methods:

(1) Dimethyl sulfate was added in small amounts to 5 g. of the material suspended in about 300 cc. of acetone and the suspension was agitated until the solid dissolved. The solution was made alkaline with sodium hydroxide to destroy excess dimethyl sulfate, and most of the acetone was removed in vacuo. A solid separated which gave a negative test for mercuric and chloride ions and reacted much like β -methoxynaphthalene. The acetone solution gave tests for mercuric and chloride ions. Evidently the $-\text{HgCl}$ radical had been severed from the naphthalene ring.

(2) Methylation with methyl chloride was not successful either. Thus after leading methyl chloride into an ether solution of 2-hydroxy-1-naphthylmercuric chloride for eight hours, no reaction had taken place. Addition of pyridine to this reaction mixture had no effect on the methylation.

(3) It was thought that bis-(-2-hydroxy-1-naphthyl) mercury might be more suitable. This compound was prepared in the same manner as 2-hydroxy-1-naphthylmercuric chloride, except that two moles of the sodium salt of β -naphthol were used to one mole of mercuric chloride. But this material was not more soluble in sodium hydroxide than 2-hydroxy-1-naphthylmercuric chloride. Furthermore when dimethyl sulfate was added to a sodium hydroxide solution of the compound, the decomposition of the dimethyl sulfate by the sodium hydroxide proceeded much faster than the methylation of the bis-(-2-hydroxy-1-naphthyl). When sufficient sulfuric acid from the decomposition of the dimethyl sulfate was formed to neutralize the remaining sodium hydroxide the original compound separated.

Grignard reaction.--The attempted preparation of 2-methoxy-1-naphthylmercuric chloride met with as little success through the Grignard reaction. 1-Bromo-2-methoxynaphthalene needed for this preparation was obtained indirectly since direct bromination of β -methoxynaphthalene is not recorded.

1-Bromo-2-naphthol was first prepared by the bromination of β -naphthol according to the directions of Franzen and Stauble.¹ One molecular equivalent of bromine dissolved in acetic acid is slowly added to a cooled, acetic acid solution of β -naphthol. The reaction mixture is poured into water and the compound which separates is crystallized from ligroin. The melting point is 82-83°. From 108 g. of β -naphthol 115 g. of 1-bromo-2-naphthol was obtained.

The methylation of 1-bromo-2-naphthol was effected by means of dimethyl sulfate. This reaction takes place very readily. The 1-bromo-2-naphthol (66 g.) was dissolved in 750 cc. of 15% potassium hydroxide and 200 cc. of dimethyl sulfate added slowly while the solution was agitated. After a short time the 1-bromo-2-methoxynaphthalene separated and was collected on a filter. It was crystallized from ligroin. Yield 75 g. The melting point of the material was 80° as compared with a melting point of 84-85° reported in the literature.

The preparation of 2-methoxy-1-naphthylmercuric chloride was then attempted by adding mercuric chloride to the Grignard reagent of 1-bromo-2-methoxynaphthalene. The preparation of this Grignard reagent presented many difficulties. The Grignard reaction can be initiated with a drop of methyl iodide. It is a very sluggish reaction, however, and the yield of Grignard reagent is very small. The 2-methoxy-1-naphthylmagnesium bromide is quite insoluble in ether. During the reaction the magnesium becomes coated with this insoluble material and prevents the reaction from going to completion. In spite of the small yield of Grignard reagent, the ether solution was filtered and treated with an ether solution of mercuric chloride. The mixture was refluxed for one and one-half hours. A small amount of white material separated which was collected on a filter. Water added to this solid in order to wash it free of excess Grignard reagent and unreacted mercuric chloride rapidly colors it a deep greenish black. The mate-

¹H. Franzen and G. Stauble, J. pr. Chem. (2) 103, 368 (1921).

rial was washed with alcohol, and the undissolved portion treated with hot acetone. Water was added to the acetone filtrate and a yellowish white material was obtained which melted sharply at 185° to a clear dark red liquid. This material gave a Beilstein test for halogen and a positive test for mercury when treated with sodium stannite. The alcohol washed material melted at 180° . These materials were not analyzed for mercury because they were obtained in insufficient quantities.

Direct mercuration.--Only one other method for the preparation of 2-methoxy-1-naphthylmercuric chloride was available, that of direct mercuration of 2-methoxynaphthalene. This method is the least satisfactory because the position of the mercury in the compound so obtained is unknown. Because of the greater reactivity of the alpha position, the entering substituent would be expected to fill that position. This for instance is true of β -naphthol whether the entering substituent is bromine or $-\text{HgC}_2\text{H}_3\text{O}_2$ radical. The question arose whether β -methoxynaphthalene would direct the entering substituent to the alpha position. Results on direct halogenation of β -methoxynaphthalene are not available and it is not certain whether the same principle would apply to the $-\text{HgC}_2\text{H}_3\text{O}_2$ radical as to the halogens. This interesting point could be settled by converting the resulting 2-methoxy-1-naphthylmercuric chloride into the corresponding 2-methoxy 1-bromonaphthalene by treatment with bromine. The only objection to this procedure is that only two methoxybromonaphthalenes are known, the 1-bromo-2-methoxynaphthalene melting at $84-85^{\circ}$ and the 6-bromo-2-methoxynaphthalene melting at $105-8^{\circ}$. However, since this was the only available method it was tried.

β -methoxynaphthalene can be easily mercurated by fusion with mercuric acetate. This can be accomplished in a short time and at a low temperature. The acetate can then be converted to the chloride by refluxing with a water solution of sodium chloride. Fusion is, however, an unsatisfactory procedure because isomers and other mercury compounds are formed. A pure material is therefore difficult to obtain especially since the naphthylmercuric chlorides are not very soluble in most solvents.

The preparation of a pure compound would be greatly facilitated if the reaction could be carried out in a solvent. Alcohol was first tried but only unreacted β -methoxynaphthalene could be recovered. Evidently the temperature afforded by this solvent was

too low for the reaction to take place. The reaction was carried out in a higher boiling solvent, acetic acid, using high concentrations of reacting materials.

The first experiments were conducted with mole per mole quantities of β -methoxynaphthalene and mercuric acetate. A mixture of 38 g. of β -methoxynaphthalene and 65 g. of mercuric acetate in 50 cc. of glacial acetic acid was refluxed gently for one and one-half hours. It gave no test for mercuric ion when treated with sodium hydroxide, indicating that all the mercuric acetate had reacted. The solution was then diluted with 200 cc. of alcohol and treated with 35 g. of calcium chloride dissolved in 100 cc. of 70% alcohol. Calcium chloride instead of sodium chloride was used because of its solubility in alcohol. The precipitate was washed with water until the washings were free of chloride ion. Both calcium chloride and unreacted mercuric acetate were removed in this manner. The material was then washed with alcohol and ether to remove the excess β -methoxynaphthalene. The material thus isolated gave a Beilstein test for halogen. Its melting point was indefinite.

Analysis: Calc. for $C_{11}H_9HgOCl$; Hg, 51.03%. Found; Hg, 57.83%, 57.31%.

The impurities may either be mercuric chloride, mercuric acetate or dimercury substituted naphthyls. Attempts at purification resulted in compounds of even higher mercury content. When the material was dissolved in hot acetone and precipitated with water its mercury content was raised to 60%. Material obtained by an acetone extraction of the compound analyzed as 59.64% and 60.36% mercury. This fraction melted sharply at $177-80^\circ$.

The preparation was repeated using mole per mole quantities of β -methoxynaphthalene and mercuric acetate. A mixture of 32 g. of the reagents in 40 cc. of glacial acetic acid was refluxed for one hour. No test for mercuric ion was obtained on treatment with sodium hydroxide as soon as the materials had dissolved in the acetic acid. The solution became yellow brown in color. It was diluted with 150 cc. of alcohol and treated with 20 g. of calcium chloride dissolved in 70 cc. of 70% alcohol. The precipitate was washed with water and then with alcohol and ether. Yield 30 g. The material gave a Beilstein test for halogen. Its melting point was $200-240^\circ$.

Analysis: Calc. for $C_{11}H_9HgOCl$; Hg, 51.03%. Found. Hg,

48.97%, 49.14%.

It is interesting to note that 2-methoxy-1-naphthylmercuric chloride is more soluble in polar than in non-polar solvents although no solvent was entirely satisfactory. Hot glacial acetic acid was unsuitable as a crystallizing agent because it decomposed the molecule. The compound is but slightly soluble in alcohol and the material obtained on using this solvent as a crystallizing agent was not pure, melting at $165-225^{\circ}$. The compound was extracted with acetone in a Soxhlet extractor and the extract evaporated to a small volume. The material obtained melted sharply at 175° . The analysis for mercury, however, showed the material to be impure.

Analysis: Calc. for $C_{11}H_9HgOCl$; Hg, 51.03%. Found; Hg, 54.36%, 54.12%, 54.32%, 53.84%.

A portion of this compound dissolved in pyridine and precipitated with alcohol showed a still higher mercury content, namely, 60.17%, 60.34%. The very great solubility of all the naphthylmercuric chlorides in pyridine is most likely due to compound formation. This reaction should yield a compound of lower mercury content but evidently the reaction is not that of simple addition. Thus, pyridine, the only reagent in which 2-methoxy-1-naphthylmercuric chloride is very soluble, is wholly unsatisfactory as a crystallizing agent.

If the higher mercury content that analysis of these preparations show is due to the formation of dimercury derivatives, perhaps their formation could be diminished by changing the ratio of β -methoxynaphthalene to mercuric acetate. The preparation was repeated in all particulars except that $2\frac{1}{2}$ moles of the ether were used to 1 mole of mercuric acetate. Although the product melted very sharply at $162-3^{\circ}$, the analysis for mercury still gave high results.

Analysis: Calc. for $C_{11}H_9HgOCl$; Hg, 51.03%. Found; Hg, 53.99%, 53.40%.

No other alternative being open, this material was used in the preparation of the unsymmetrical mercury derivative. The procedure was somewhat justified on the ground that the dimercury derivatives would not react with the Grignard reagent and their insolubility in the ether would exclude them from the reaction.

The proof of the position of the $-HgCl$ radical was attempted by refluxing the 2-methoxy-1-naphthylmercuric chloride with

bromine and potassium bromide in chloroform solution. A small amount of material was obtained which when crystallized from ligroin melted at 80° and had the outward appearance of 1-bromo-2-methoxynaphthalene. This experiment does not conclusively prove the position of the -HgCl radical since only two bromomethoxynaphthalenes are known but it indicates that the -HgCl radical is probably in the alpha position.

UNSYMMETRICAL ORGANOMERCURY COMPOUNDS

Since the same general method of preparation was used for all the unsymmetrical organomercury compound, it will be described in detail and any changes or peculiarities arising in the preparation of any one compound will be described separately when that particular compound is discussed. The method used was that of treating a Grignard reagent with an organomercuric chloride.

Kharasch and Marker state in their paper that the failure of earlier investigators to obtain unsymmetrical organomercury compounds was due to the use of too great an excess of Grignard reagent and to heating the mixture after the organomercuric chloride had been added. Only 2-2 1/2 moles of Grignard reagent to 1 mole of organomercuric chloride was used, but efforts to avoid the second pitfall led to difficulties. Because heat disproportionated the unsymmetrical molecule into two symmetrical ones, Kharasch and Marker conducted their reactions at 5° . Most of their reactions consisted in treating a Grignard reagent with alkyl- or phenylmercuric halides. When reactions in the naphthalene series were attempted at this low temperature, the Grignard reagent precipitated and the reaction proceeded very slowly. For this reason the preparations of the unsymmetrical organomercury compounds were carried out at about 20° .

Because of the work of Hilpert and Grüttner, the Grignard reagent of the radical anticipated to be more electronegative was prepared. The procedure was as follows: Two and one-half moles of the Grignard reagent was prepared in a special Grignard flask. The bottom of this flask was fitted with a sintered glass filter and a stopcock to facilitate filtering the Grignard reagent. The insolubility of the Grignard reagents of the naphthalene series necessitated a few changes in the standard procedure for their preparation in order to obtain a good yield. A fairly large volume

of ether was used and stirring was at times avoided. Heating was resorted to in cases where the reaction was sluggish. When the reaction had gone to completion the ether solution was filtered from the unchanged magnesium through the sintered glass filter into another Grignard flask. The flask was immersed in a beaker of tap water and the arylmercuric chloride added a little at a time until it dissolved. The unsymmetrical compounds in most cases were not very soluble in the ether. When precipitation started, the addition of arylmercuric chloride was stopped even though the theoretical amount had not yet been added. The mixture was then poured over ice and water and the excess Grignard decomposed with 1% sulfuric acid. The temperature was not allowed to rise above 10°. When the compound was soluble in ether, the mixture was extracted with this solvent and the extract dried with sodium sulfate. The filtrate was evaporated to a small volume in vacuo or in a stream of dry air and the solid washed with absolute alcohol and ether. Usually the compound was only slightly soluble in ether. In that case the ether fraction, after the decomposition of the excess Grignard, was separated and treated as described above. The solid undissolved was collected on a filter, washed with water acidulated slightly with sulfuric acid and where possible crystallized from some solvent. Because of the instability of the unsymmetrical compounds, this crystallization was performed in the cold. At times even this purification was not feasible.

The compound obtained was then treated in the following manner.

1. The first step was to analyze the material. If the calculated mercury content was obtained the other steps were performed.

2. A portion of the material, usually 0.5-1 g., was treated with mercuric chloride and an attempt was made to separate and identify the two arylmercuric chlorides formed. The unsymmetrical compound was dissolved in benzene and the mercuric chloride dissolved in alcohol. The procedure used after the two solutions were mixed was adapted to the individual substances involved. Benzene was used as the solvent because of the greater solubility of all types of naphthyl mercury compounds in it. Sometimes the solvent was evaporated and the mixture of arylmercuric chlorides extracted with suitable solvents. In other cases fractional crystallization of the benzene solution was resorted to. When the two

arylmercuric chlorides had melting points very close together and when their solubilities were similar, the mixture of arylmercuric chlorides was analyzed for mercury. The mercury content so obtained was compared with the theoretically calculated mercury content of an equimolecular mixture of the two arylmercuric chlorides in question.

3. The crucial test and the one for which these compounds were prepared was then applied, that of cleavage with hydrogen chloride. For this reaction the unsymmetrical compound was dissolved in benzene and a few drops of alcoholic hydrogen chloride added. The solvent was then evaporated to dryness in a stream of air, the solid washed with ligroin to dissolve the hydrocarbons or the substituted hydrocarbons, the material dried and then analyzed for mercury. From this analysis the amount of each arylmercuric chloride was calculated. The relative electronegativity of the radicals involved was then deduced.

Although Kharasch and Marker warmed the mixture after the addition of hydrogen chloride, this procedure was not used because in some cases the excess hydrogen chloride with the aid of heat further attacked the arylmercuric chloride, yielding incorrect results.

The method of removing the hydrocarbons or substituted hydrocarbons was also a problem. At first it was thought that steam distillation would remove the naphthalene, halogenated naphthalene, benzene and excess hydrogen chloride. However, this procedure was not only time consuming, but the steam distillation proved in one compound to completely reverse the order of cleavage.

I. α -Naphthyl Mercury β -Naphthyl

α -Naphthyl mercury β -naphthyl was prepared from α -naphthylmagnesium bromide and β -naphthylmercuric chloride. It is a white substance, somewhat soluble in benzene but only to a small extent in ether. It melts at 175° .

Analysis: Calc. for $C_{20}H_{14}Hg$; Hg, 44.12%. Found; Hg, 44.62%, 43.96%.

Treatment with mercuric chloride.--Cleavage with mercuric chloride was accomplished in the manner described above. Separation of the α - and β -naphthylmercuric chlorides was accomplished by fractional crystallization of the benzene solution. The melting point of the material first precipitated from solution was

261°, evidently impure β -naphthylmercuric chloride. The second fraction melted at 165°, evidently impure α -naphthylmercuric chloride. Both of these materials were crystallized from hot benzene. The melting point of the first fraction was 268°. Pure β -naphthylmercuric chloride melts at 271°. The melting point of the second fraction was 185-6°. Pure α -naphthylmercuric chloride melts at 188°. The separation in this case was quite easy because the melting point difference between the two organomercuric chlorides was large and their solubility in benzene sufficiently different.

Treatment with hydrogen chloride.--The cleavage with hydrogen chloride was accomplished in the manner already described. When the benzene was evaporated to dryness and the mixture washed with ligroin and dried, the melting point of the solid was 230°. Since both α - and β -naphthylmercuric chloride have the same mercury content, analysis of the mixture was accomplished by means of a melting point curve. This graph was made by determining the melting points of various mixtures of α - and β -naphthylmercuric chlorides. The composition of a mixture of any melting point could then be read from the graph. In this manner it is seen that a mixture whose melting point is 230° consists of 30% α -naphthylmercuric chloride and 70% β -naphthylmercuric chloride. This indicates that the α -naphthyl radical is more electronegative than the β -naphthyl radical.

In another preparation the unsymmetrical compound melted at 173-5° after the crude material had been purified by dissolving in chloroform.

Analysis: Calc. for $C_{20}H_{14}Hg$; Hg, 44.12%. Found; Hg, 42.94%, 42.91%.

A portion of the ether solution of the unsymmetrical compound was treated with alcoholic hydrogen chloride even before the material was isolated. The melting point of the mixture so obtained was 235-6°. This corresponds to 80% of β -naphthylmercuric chloride and 20% α -naphthylmercuric chloride.

The cleavage of the compound isolated from this preparation with hydrogen chloride in the usual manner yielded a material which again melted at 230°. This melting point corresponds to a mixture of 70% β -naphthylmercuric chloride and 30% α -naphthylmercuric chloride.

A portion of this material was dissolved in ether and

treated with alcoholic hydrogen chloride. The solid obtained was washed with ligroin. The melting point of this material was 223° which corresponds to a mixture consisting of 75% β -naphthylmercuric chloride and 25% α -naphthylmercuric chloride. These results are all in accord with the conclusion that the α -naphthyl radical is more electronegative than the β -naphthyl radical.

It seems strange, however, that when a benzene solution of α -naphthyl mercury β -naphthyl is saturated with hydrogen chloride and steam distilled, the solid isolated has a melting point of $156-85^{\circ}$. This melting point corresponds to a mixture consisting of 70% α -naphthylmercuric chloride and 30% β -naphthylmercuric chloride. This is a complete reversal of the previous results. The amounts of material recovered from this distillation indicated no destruction of aryl chloride.

II. 4-Chloro-1-naphthyl Mercury α -Naphthyl

This unsymmetrical compound was prepared from α -naphthylmagnesium bromide and 4-chloro-1-naphthylmercuric chloride in the manner already described. The Grignard reagent should not be cooled as it will precipitate. The unsymmetrical compound is almost insoluble in ether. The material was extracted with benzene from the reaction mixture. It melted at $185-90^{\circ}$.

Analysis: Calc. for $C_{20}H_{13}HgCl$; Hg, 41.03%. Found; Hg, 41.12%, 41.06%.

Treatment with mercuric chloride.--Since the melting points of the two organomercuric chlorides resulting from the mercuric chloride cleavage would be quite different, a separation of the two was attempted by fractional crystallization from the benzene solution. It was expected that the 4-chloro-1-naphthylmercuric chloride would be less soluble in benzene than α -naphthylmercuric chloride and would precipitate first. The first fraction obtained melted at 210° which after two crystallizations from hot benzene melted at 242° . The melting point of pure 4-chloro-1-naphthylmercuric chloride is $239-40^{\circ}$. Further evaporation of the benzene solution yielded a material which melted at 186° . This is evidently α -naphthylmercuric chloride. Pure α -naphthylmercuric chloride melts at 188° .

Treatment with hydrogen chloride.--This unsymmetrical mercurial was treated in the following manner.

1. Dry hydrogen chloride was passed into a suspension of

the unsymmetrical compound in benzene until the material dissolved. The solution was then steam distilled. The dried residue had a melting point of $185-7^{\circ}$.

Analysis: Found; Hg, 51.60%, 51.72%, 51.57% which corresponds to 75% 4-chloro-1-naphthylmercuric chloride.

2. The unsymmetrical compound was dissolved in ether and alcoholic hydrogen chloride was added. The solvent was evaporated in a stream of air and the solid obtained washed with a small quantity of ether and dried. The melting point of the mixture was $185-93^{\circ}$.

Analysis: Found; Hg, 51.61%, 50.81%. The average of these analyses indicates a mixture consisting of 84% 4-chloro-1-naphthylmercuric chloride and 16% α -naphthylmercuric chloride. These results both show that the α -naphthyl radical is more electronegative than the 4-chloro-1-naphthyl radical.

III. 4-Chloro-1-naphthyl Mercury Phenyl

This unsymmetrical compound was prepared from phenylmagnesium bromide and 4-chloro-1-naphthylmercuric chloride. The melting point of the compound was $168-70^{\circ}$.

Analysis: Calc. for $C_{16}H_{11}HgCl$; Hg, 45.65%. Found; Hg, 44.95%, 44.90%.

Treatment with mercuric chloride.--The cleavage with mercuric chloride was accomplished in the manner described. Since the melting points of 4-chloro-1-naphthylmercuric chloride and phenylmercuric chloride differ by only a few degrees and especially since their solubilities are much alike, their separation could not be accomplished. The solution of the mixture was evaporated in a stream of air. The solid obtained was washed with water to remove any excess mercuric chloride and dried. The melting point of this material was 194° .

Analysis: Calc. Hg, 56.30%. Found; Hg, 56.19%, 56.16%.

Treatment with hydrogen chloride.--The general procedure described was employed in this cleavage. The melting point of the mixture was 195° .

Analysis: Found; Hg, 57.72%, 58.14%. The average of these analyses is equivalent to a mixture containing 38% of 4-chloro-1-naphthylmercuric chloride and 62% phenylmercuric chloride.

A portion of the dried ether extract of the unsymmetrical compound obtained from the Grignard reagent, before the isolation

of the compound, was treated with a few drops of alcoholic hydrogen chloride. The ether solution was evaporated in a stream of air, the solid washed with ligroin and dried. It melted at $193-6^{\circ}$. Analysis showed it to contain 58.34% mercury. This mercury content is equivalent to a mixture containing 35% 4-chloro-1-naphthylmercuric chloride and 65% phenylmercuric chloride. These results indicate that the 4-chloro-1-naphthyl radical is more electronegative than the phenyl radical.

IV. 5-Bromo-1-naphthyl Mercury-1-naphthyl

This unsymmetrical compound was prepared from α -naphthylmagnesium bromide and 5-bromo-1-naphthylmercuric chloride. The compound melted at 144° .

Analysis: Calc. for $C_{20}H_{13}HgBr$; Hg, 37.57%. Found; Hg, 37.97%, 37.20%.

Treatment with mercuric chloride.--Since the melting points of the two resulting arylmercuric chlorides, namely α -naphthylmercuric chloride and 5-bromo-1-naphthylmercuric chloride differ by over 50° , it was thought possible to separate them from the mixture. The solution resulting from the cleavage was evaporated to dryness in a stream of air. The melting point of the solid obtained was 173° . The solid was extracted with cold acetone. The melting point of the residue was $220-227^{\circ}$. The acetone filtrate was evaporated to dryness. The melting point of this solid was $155-65^{\circ}$. Both of these fractions were crystallized from hot benzene. The melting point of the acetone fraction was 227° . Pure 5-bromo-1-naphthylmercuric chloride melts at 228° . The second fraction melted at $185-6^{\circ}$. Pure α -naphthylmercuric chloride melts at 188° .

Treatment with hydrogen chloride.--This cleavage was accomplished in the manner described. The melting point of the solid obtained was 188° .

Analysis: Found; Hg, 47.73%, 48.38%. The average of these analyses corresponds to a mixture containing 25% of α -naphthylmercuric chloride and 75% 5-bromo-1-naphthylmercuric chloride. This indicates that the α -naphthyl radical is more electronegative than the 5-bromo-1-naphthyl radical.

V. 2-Methoxy-1-naphthyl Mercury-1-naphthyl

An attempt was made to prepare this compound from 2-methoxy-1-naphthylmagnesium bromide and α -naphthylmercuric chloride,

but owing to difficulties in the preparation of the Grignard reagent, the compound was not obtained.

This unsymmetrical compound was prepared from α -naphthylmagnesium bromide and 2-methoxy-1-naphthylmercuric chloride in the manner described. This material is very unstable and must be isolated quickly, since it becomes purple on contact with moisture. It melts at 209° .

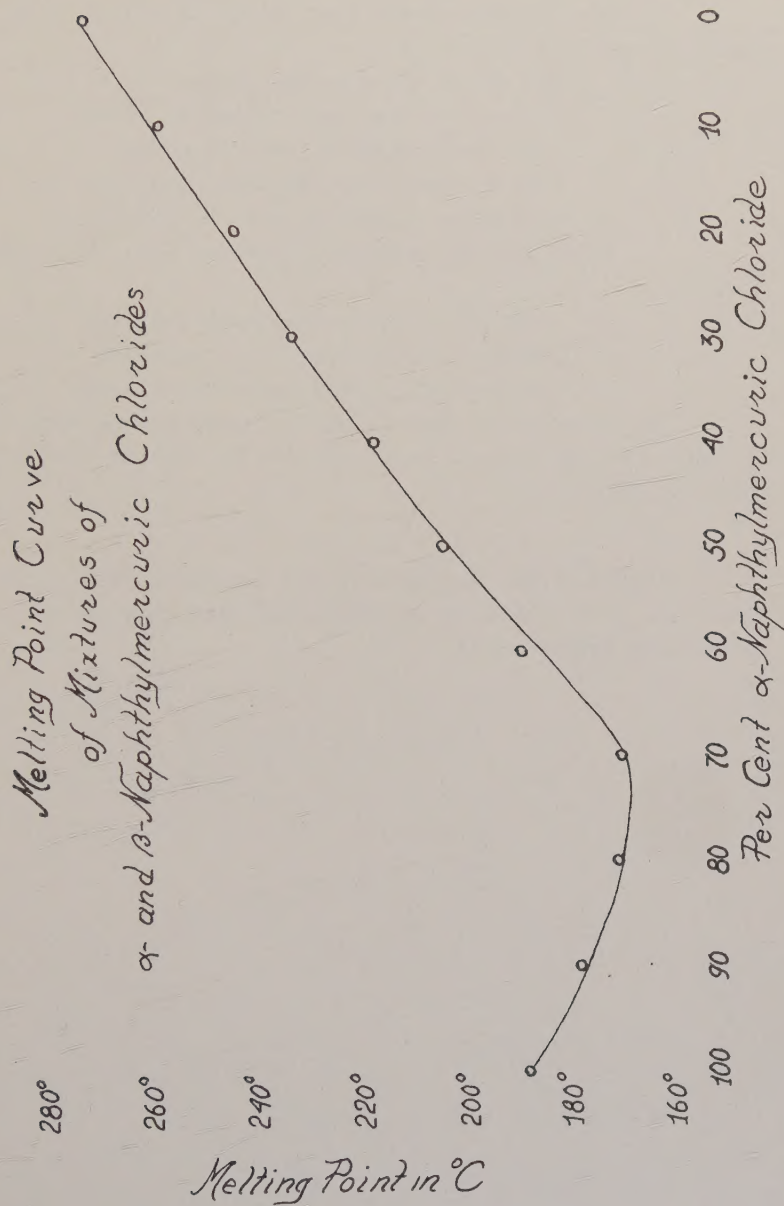
Analysis: Calc. for $C_{21}H_{13}OHg$; Hg, 41.38%. Found; Hg, 42.02%, 42.20%, 41.76%.

Treatment with mercuric chloride.--Because of the difficulty of separating the two resulting organomercuric chlorides, the benzene solution containing them was evaporated to dryness. The melting point of the solid obtained was $135-60^{\circ}$.

Analysis: Calc. Hg, 53.19%. Found; Hg, 53.38%, 53.10%.

Treatment with hydrogen chloride.--This was accomplished in the manner described. The material obtained melted at $175-6^{\circ}$ to a dark red liquid.

Analysis: Found; Hg, 53.54%, 54.36%. These analyses correspond to mixtures containing 39% and 16% respectively of 2-methoxy-1-naphthylmercuric chloride. The average is 27%, thus indicating that the 2-methoxy-1-naphthyl radical is more electronegative than the α -naphthyl radical.



SUMMARY

1. The electronegativities of the radicals in the following compounds were compared:

α -Naphthyl mercury β -naphthyl

4-Chloro-1-naphthyl mercury α -naphthyl

4-Chloro-1-naphthyl mercury phenyl

5-Bromo-1-naphthyl mercury α -naphthyl

2-Methoxy-1-naphthyl mercury α -naphthyl

2. Three new organomercuric halides were prepared. They are:

4-Chloro-1-naphthylmercuric chloride

5-Bromo-1-naphthylmercuric chloride

2-Methoxy-1-naphthylmercuric chloride

3. Conclusions drawn from the study of the effect of substituents on the benzene ring may also be applied in the naphthalene series.

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